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By

BEN H. PETERSON

B.S. Coe College, 1918
M.S. The State University of Iowa, 1922

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE COLLEGE OF THE STATE UNIVERSITY OF IOWA, JUNE, 1926

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ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Dr. Edward Bartow under whose direction this investigation was carried out. He also hereby expresses his thanks to Dr. J. N. Pearce for his many suggestions and kindly encouragement.

Effect of Salts on the Rate of Coagulation and the Optimum Precipitation of Alum Floc[1]

Ben H. Peterson and Edward Bartow

THE STATE UNIVERSITY OF IOWA, IOWA CITY, IA.

THE properties of the alum floc used in water purification have long been subjects of investigation. The composition of the floc is not definitely known though it is usually written as $Al(OH)_3$. It is a gelatinous substance, highly adsorptive, amphoteric, and relatively insoluble over a wide range of hydrogen-ion concentration. Miller[2] has shown that the composition varies if the precipitate is formed in the presence of different ions, owing either to the adsorption of the ions or to the formation of a basic salt. Williamson,[3] Bancroft,[4] and Rose[5] have isolated basic salts by partially neutralizing a solution of an aluminum salt with various alkalies. Miller[6] has further shown, by the precipitation of an alum floc from a solution containing oxalate and sulfate ions, that the ratio of the oxalate and sulfate ions in the precipitate is dependent upon their concentration in the solution. This strongly suggests a true adsorption phenomenon. Charriou[7] showed that divalent ions carried down by the precipitate could be displaced by ions of a higher valence, further indicating adsorption. It is possible that the variation of composition under varying conditions might be due to both adsorption and a complex salt formation. This factor has not been carefully considered in the investigations of the properties of the floc. Obviously the precipitate formed in the presence of various salts would show different properties, such as the rate of coagulation, conditions of optimum precipitation, etc.

The factor most consistently investigated has been the so-called optimum hydrogen-ion concentration for coagulation. If the floc is an ampholyte it should exhibit a point of maximum insolubility—i. e., a hydrogen-ion concentration at which the solubility of the floc is least. As the pure floc is colloidal in most of its properties, it should show its

[1] Received August 15, 1927. Abstract of a thesis submitted by Ben H. Peterson in partial fulfilment of the requirements for the degree of doctor of philosophy in the State University of Iowa.

[2] *U. S. Pub. Health Service, Pub. Health Repts.*, **32**, 1895 (1925).

[3] *J. Phys. Chem.*, **27**, 284 (1923).

[4] *Ibid.*, **26**, 501 (1923).

[5] *Kolloid-Z.*, **15**, 1 (1924).

[6] *U. S. Pub. Health Service, Pub. Health Repts.*, **40**, 1502 (1924).

[7] *Compt. rend.*, **176**, 679 (1923).

least stability at the same point. This isoelectric point has been reported by different investigators at values ranging from 4.90 to 7.20. Baylis[8] and Norcum[9] report optimum values for coagulation distinctly on the acid side of neutrality, adjusting to this value by treating the water with sulfuric acid. This was tried by the writer at the Cedar Rapids, Ia., plant, and the conditions and rate of formation of the floc did improve. Bates,[10] at the writers' suggestion, substituted an equivalent quantity of sodium sulfate and obtained identical results without affecting the hydrogen-ion concentration to any measurable degree. Theriault and Clark[11] found optimum conditions for coagulation at a pH value of 4.9 to 5.4, using 100 to 400 p. p. m. of alum in solutions buffered with phosphates. This is in accord with the observations of Baylis and Norcum, but will be further discussed later in this paper.

It becomes evident, therefore, that any attempt to establish optimum coagulation conditions must take into consideration the effect of the salts present in the water. Whether the ions of such salts are adsorbed or form a basic salt precipitate, the properties of the resultant floc will vary according to the kind and concentration of such salts. This investigation was then planned to determine what some of the effects might be, and if the salts normally present in water supplies did affect the conditions of optimum floc formation. It is not expected that all the observations and conclusions included will have a direct application to waterworks practice. Salts have been used which do not occur in natural waters, but have been included in an attempt to establish general principles which would clarify some of the conflicting ideas concerning the properties and actions of alum floc in waterworks practice.

Experimental

The coagulation experiments were performed in 300-cc. bottles of a good quality of clear glass. The solutions to be tested were placed in the bottles in a shaking rack and rotated 22 r. p. m. This was not violent enough to break the floc after it was formed. Tests to determine the effect of small variations in the rate of rotation showed no measurable effect between 20 and 30 r. p. m. A dilute solution of sodium hydroxide was added to the solutions in increasing amounts to each bottle, the quantity being determined by experience. The alkali was added slowly just below the surface of the liquid with care to prevent mixing during the addition. Further tests to determine whether the time elapsed between the addition of the reagents and the beginning of the shaking had any effect showed no measurable difference up to the limit of the experiments.

[8] *J. Am. Water Works Assocn.*, **10**, 563 (1921).
[9] *Ibid.*, **11**, 97 (1924).
[10] Personal communication.
[11] *U. S. Pub. Health Service, Pub. Health Repts.*, **38**, 181 (1923).

The bottles were placed in the stirrer as quickly and with as little agitation as possible. The tests were made in a darkened room and the conditions of the suspension of the floc observed by allowing a beam of light from a 100-watt lamp passing through a $^3/_4$-inch (1.6-cm.) tube 3 inches (7.6 cm.) long to fall upon the bottle, the observations being made from an angle to the beam. The Tyndall cone so produced was very well defined and the coagulation of the floc particles could be plainly seen. The change from a bright cone to a flocc ondition was very abrupt and could be duplicated within a few seconds in successive experiments. Observations were made at half-minute intervals at the beginning of the experiment until the more quickly coagulated samples were flocculated and then at intervals dictated by experience. On the acid side of coagulation the floc was always opaque and well-defined, but on the alkaline side it was more glassy in appearance and the time of coagulation was not so easily observed, especially at low concentrations of the salts.

The alum solution used was made by dissolving 6.84 grams of recrystallized aluminum sulfate of the formula $Al_2(SO_4)_3 \cdot 16H_2O$ in 1 liter of distilled water. This was of such a strength that 1 cc. added to 200 cc. of water was equivalent to 2 grains per gallon (34 p. p. m.). Such a concentration represents about an average filter-plant dosage. In the sulfate experiments the solution was made up of aluminum chloride of equivalent concentration. The salts to be added were made up in such concentration that 1 cc. of the solution added to 200 cc. of the sample was equivalent to 20 p. p. m. expressed as calcium sulfate. The required amount of alum and the additional salt were placed in a 2-liter flask, diluted with distilled water to the mark, well mixed, and 200 cc. of this solution placed in each of the bottles. The alkali was then added in varying amounts, the rotation begun, and the observations made as described above. The pH of the solutions was determined colorimetrically.

Results

Sodium Sulfate—The effect of sodium sulfate is shown in Table I and Graph No. I. The sulfate content of a 2-grains per gallon (34 p. p. m.) dose of filter alum is equivalent to about 20.9 p. p. m. as $CaSO_4$. The results plotted in the first curve, then, show the effect of slightly more than the sulfate which would be added with 2 grains per gallon (34 p. p. m.) of filter alum. This shows a maximum coagulation at about 7.3 to 7.4 and coagulation within a reasonable length of time is between rather narrow limits. Further additions of the sulfate produced a marked effect, lowering somewhat the time required for coagulation, but not proportionately, and widening the zone of coagulation to the acid side. The effect is more marked between 25 and 100 p. p. m. than between 100 and 500 p. p. m. Water of sulfate content corresponding to 100 p. p. m. would be considered only moderately

hard, and most public supplies of the Middle West would equal or exceed that amount. If, then, other factors did not influence the formation of the floc, it would form readily within a pH range of 6.0 and 7.5, with perhaps the optimum conditions at 6.75.

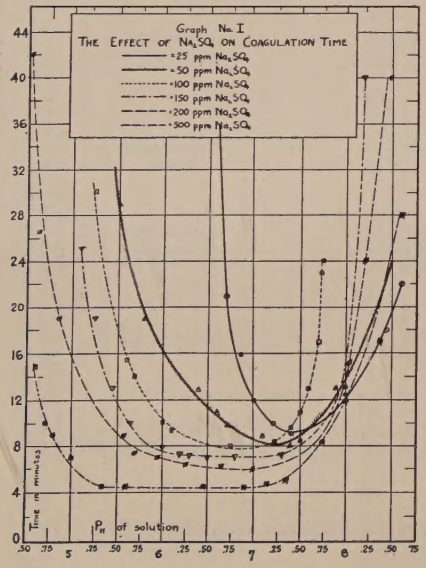
Table I—Effect of Sodium Sulfate on Time Required for Coagulation of Alum Floc, Using Aluminum Chloride Solution and Adjusting Alkalinity with Sodium Hydroxide

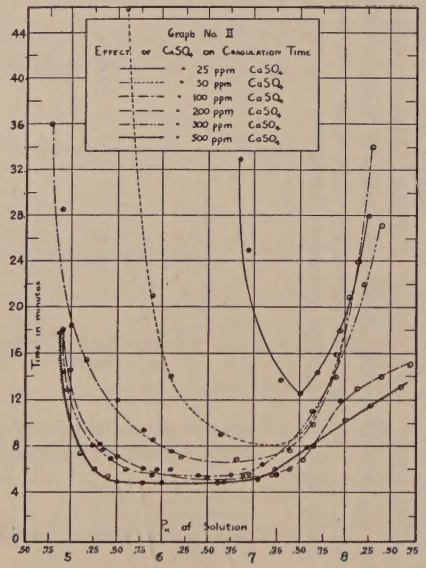
Na_2SO_4—25 P. P. M.		Na_2SO_4—50 P. P. M.		Na_2SO_4—100 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.30	46	5.5	29	5.25	39
6.60	36	5.8	19	5.60	15.5
6.70	31	6.0	16	5.70	14
6.85	16	6.4	13	6.00	10
7.00	12	6.6	11	6.10	9.5
7.20	10	6.7	10	6.75	8
7.40	9	7.1	9	7.20	8.5
8.00	12.5	7.4	8	7.40	9.5
8.45	18	7.9	13	7.50	11
8.60	22	8.3	19	7.60	13
		8.5	24	7.70	17
				7.72	23
				7.75	26
				8.10	33
				8.35	48

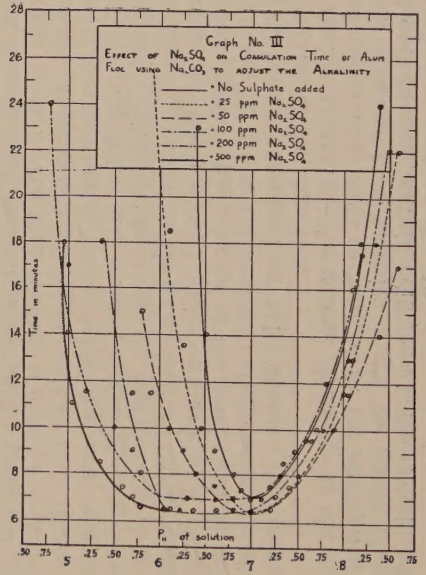
Na_2SO_4—150 P. P. M.		Na_2SO_4—200 P. P. M.		Na_2SO_4—500 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.10	25	4.50	42	4.60	15
5.25	19	4.60	26.5	4.70	10
5.45	13	4.85	19.5	4.80	9
5.65	10	5.45	9.5	5.00	7
5.70	9	5.60	9	5.50	4.5
5.75	8	5.70	8.5	5.60	4.5
5.85	8	5.95	6.5	6.45	4.5
6.00	8	6.25	6.5	6.90	4.5
6.20	7.5	6.65	6.5	7.15	4.75
6.30	7.5	7.00	6	7.35	5
6.50	7	7.75	8.5	7.60	9
6.80	7	8.05	15	8.00	12
7.30	7	8.20	24	8.40	17
7.50	8.5	8.25	42	8.60	28
7.80	10				
8.00	15				
8.20	40				

Calcium Sulfate—These experiments using calcium instead of sodium sulfate as the source of the added sulfate ion were tried to determine whether the positive ion would have any effect on the rate of coagulation. Alum floc, being a positive colloid, is stabilized by positive ions. If the calcium ion is adsorbed to a different degree of effectiveness than the sodium ion, a difference in the coagulative properties of their sulfates would be apparent. In general, little difference is shown by a comparison of the curves in Graphs Nos. I and II, a concentration of equivalent sulfates extending the zone of rapid coagulation to about the same degree. Although there can be no doubt that the sodium and calcium ions do exert a different stabilizing influence, the difference is negligible in this particular case.

Sodium Sulfate, Adjusting Alkalinity with Sodium Carbonate—On account of the similarity of the sulfate and carbonate ion it would seem probable that the carbonate ion would have an additive effect and that the result would be as if a larger quantity of the sulfate were used. In general, however, there is no noticeable effect and the results (Table III and Graph No. III) are similar to those in which


Graph No. I
THE EFFECT OF Na_2SO_4 ON COAGULATION TIME
= 25 ppm Na_2SO_4
= 50 ppm Na_2SO_4
=100 ppm Na_2SO_4
=150 ppm Na_2SO_4
=200 ppm Na_2SO_4
=300 ppm Na_2SO_4
Time in minutes
P_H of solution


Graph No. II
EFFECT OF $CaSO_4$ ON COAGULATION TIME
= 25 ppm $CaSO_4$
= 50 ppm $CaSO_4$
= 100 ppm $CaSO_4$
= 200 ppm $CaSO_4$
= 300 ppm $CaSO_4$
= 500 ppm $CaSO_4$
Time in minutes
P_H of Solution


Graph No. III
EFFECT OF Na_2SO_4 ON COAGULATION TIME OF ALUM FLOC USING Na_2CO_3 TO ADJUST THE ALKALINITY
= No Sulphate added
= 25 ppm Na_2SO_4
= 50 ppm Na_2SO_4
= 100 ppm Na_2SO_4
= 200 ppm Na_2SO_4
= 500 ppm Na_2SO_4
Time in minutes
P_H of solution

the hydroxide was used to adjust the alkalinity. There was no attempt to correct for the sulfate added as the alum.

Table II—Effect of Calcium Sulfate on Time Required for Coagulation of Alum Floc, Using Aluminum Chloride Solution and Adjusting Alkalinity with Sodium Hydroxide

$CaSO_4$—25 p. p. m.		$CaSO_4$—50 p. p. m.		$CaSO_4$—100 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.85	33	5.60	46	4.75	36
6.95	25	5.90	21	4.90	28.5
7.30	13.5	6.10	14	5.00	18.5
7.50	12.5	6.65	9	5.15	15.5
7.70	14.5	7.40	8	5.50	12
7.93	18	8.00	18	5.80	9.5
8.25	25	7.70	13	5.90	8.5
		8.05	21	6.10	7.5
				6.20	7
				6.80	7
				7.40	7
				7.65	10
				7.90	14
				8.15	24
				8.30	34

$CaSO_4$—200 p. p. m.		$CaSO_4$—300 p. p. m.		$CaSO_4$—500 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
4.90	18	4.90	17	4.90	17.5
5.30	8	5.00	14.5	4.95	14.5
5.35	7.5	5.15	8.5	5.00	13
5.50	7	5.25	8	5.10	7
5.80	6	5.45	7	5.25	6
5.96	6	5.90	5.5	5.40	5.5
6.10	5.5	5.60	6	5.50	5
6.40	5.5	6.50	5.5	5.80	5
6.65	5.5	6.90	5.5	6.00	5
6.75	5.5	7.10	6.5	6.50	5
6.95	5.5	7.40	8	6.65	5
7.20	5.5	7.65	11	7.05	5
7.25	5.5	7.90	16	7.20	6
7.40	6	8.20	22	7.60	8
7.55	7	8.40	27	8.00	10.5
7.65	8			8.30	11.5
7.95	12			8.60	13.5
8.15	13			8.70	14.5
8.40	14				
8.70	15				

Ferrous Sulfate—Ferrous sulfate has long been used alone and with alum in water purification. In waters of high turbidity and low color its use has decreased the amount of alum necessary to effect clarification. These experiments (Table IV and Graph No. IV) show a very decided effect even in such small concentrations as 0.5 grain per gallon (8.5 p. p. m.). The time interval is lowered by one-third and the pH range is extended from 5.0 to 7.5. It would at first appear that ferrous sulfate would be an ideal coagulation aid in waters of low salt content, especially colored waters, it having been shown that colors are best removed in an acid medium; but unfortunately such colors are usually tannates, which form highly colored bodies with iron salts. The difference between the behavior of the ferrous and the sodium salts may be due to the formation of the hydroxide of iron at the higher concentrations, which affords a nucleus for the formation of the alum floc.

Sodium Oxalate—The general similarity of the sulfate and oxalate ions would perhaps justify the assumption that their behavior in coagulation would be nearly identical. There is, however, a distinct difference in their relative effects. (Table V and Graph No. V) Concentrations up to 5 or 10 p. p. m. do show a decrease in the time required for coag-

Graph No. IV
Effect of $Fe_2(SO_4)_3$ on Coagulation
Alum alone 34 p.p.m.
5 ppm $Fe_2(SO_4)_3$
10 ppm $Fe_2(SO_4)_3$
20 ppm $Fe_2(SO_4)_3$
50 ppm $Fe_2(SO_4)_3$
Time in minutes
P_H of solution

Graph No. V
Effect of $Na_2C_2O_4$ on Coagulation
Alum alone 34 p.p.m.
5 ppm Sodium Oxalate
10 ppm Sodium Oxalate
20 ppm Sodium Oxalate
Time in minutes
P_H of Solution

Graph No. VI
Effect of Potassium Tartrate on Coagulation Time
5 ppm Tartrate
25 ppm Tartrate
10 ppm Tartrate
Time in minutes
P_H of solution

ulation and extend the zone of rapid coagulation up to a pH of about 6.0. An increase to 20 p. p. m., however, behaves very differently. The coagulation is slowed down and confined within very narrow pH limits—from 7.0 to 7.5. The significance of this specific action must lie in the formation of a basic oxalate compound with the alum floc, with resultant properties very different from those of the floc alone.

Table III—Effect of Sodium Sulfate on Coagulation Time of Alum Floc, Using Aluminum Sulfate and Adjusting Alkalinity with Sodium Carbonate

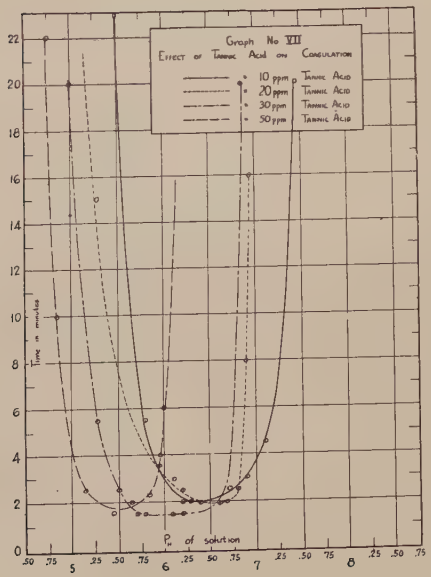
Na_2SO_4—000 P. P. M.		Na_2SO_4—25 P. P. M.		Na_2SO_4—50 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.30	31	5.90	25.5	5.80	15
6.40	23	6.10	18.5	5.90	11.5
6.50	14	6.25	13.5	6.10	10
6.80	8	6.45	10	6.25	9
6.85	7.5	6.60	9	6.40	8
7.10	7	6 80	7	6.50	7.5
7.20	7.15	6.85	6.5	6.90	6.5
7.30	8	6.90	6.5	7.00	6.5
7.45	9	7.15	6.5	7.20	6.5
7.70	11	7.50	8	7.40	7.5
8.00	14	7.75	10	7.90	10
8.10	16	8.00	11.5	8.05	11.5
8.40	24	8.10	13	8.50	15
		8.35	18	8.60	17.5
		8.60	22		

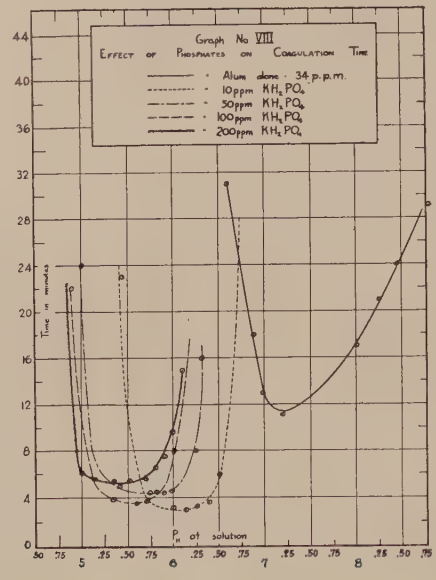
Na_2SO_4—100 P. P. M.		Na_2SO_4—200 P. P. M.		Na_2SO_4—500 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.35	18	4.5	24	4.9	24
5.70	11.5	5.0	14	4.95	23
6.10	6.5	5.2	11.5	5.0	17
6.35	6.5	5.5	10	5.05	11
6.60	6.5	5.7	9	5.35	8.5
6.80	6.5	5.8	8	5.6	7.15
7.00	6.5	6.0	7	5.7	6.5
7.20	7	6.3	7	5.8	6.5
7.65	9.5	6.6	7	6.05	6.5
7.95	11	6.6	7	6.35	6.5
8.05	13	7.0	7	6.4	6.5
8.20	18	7.2	7	6.6	6.5
8.50	22	7.35	8.5	6.95	6.5
		7.6	9.5	7.1	6.5
		7.8	12	7.25	7
		8.2	17.5	7.5	12
				7.9	17 5

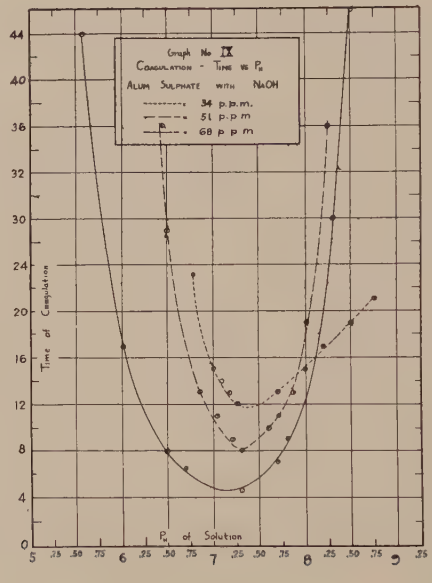
Table IV—Effect of Ferrous Sulfate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

$FeSO_4$— 000 P. P M.		$FeSO_4$— 10 P. P. M.		$FeSO_4$— 25 P. P. M.		$FeSO_4$— 50 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.8	23	5.8	36	5.0	23.5	4.5	35
7.0	15	5.95	26	5.2	15.5	4.6	14
7.1	14	6.15	17	5.3	14	4.65	12
7.2	13	6.2	14.5	5.4	12	4.75	10
7.25	12	6.4	11.5	5.7	8	5.0	6
7.7	13	6.6	6	6.0	5	5.3	4
8.0	15	7.0	4	6.2	4.5	5.4	3.5
8.2	17	7.2	4	6.4	3.5	5.6	3
8.5	19	7.8	6	6.5	3	6.2	2
8.75	21	8.2	11.5	7.15	3	6.6	2
		8.6	23	7.6	3	7.1	2
		9.0	33	8.0	5	7.2	2
				8.25	7.5	7.9	3
				8.5	11	8.3	6
						8.5	8
						8.6	30

Potassium Tartrate—The effect of the tartrate ion is comparable with that of the oxalate ion. (Table VI and Graph No. VI) Low concentrations of the tartrate change the coagulation curves decidedly, moving the point of opti-


Graph No VII
Effect of Tannic Acid on Coagulation
10 ppm Tannic Acid
20 ppm Tannic Acid
30 ppm Tannic Acid
50 ppm Tannic Acid
Time in minutes
Pₕ of solution


Graph No VIII
Effect of Phosphates on Coagulation Time
Alum alone - 34 p.p.m.
10 ppm KH₂PO₄
30 ppm KH₂PO₄
100 ppm KH₂PO₄
200 ppm KH₂PO₄
Time in minutes
Pₕ of solution


Graph No IX
Coagulation - Time vs Pₕ
Alum Sulphate with NaOH
34 p.p.m.
51 p.p.m
68 p p m
Time of Coagulation
Pₕ of Solution

mum coagulation over to the acid side. Five parts per million give the optimum point at 6.5; 7.5 p. p. m. place it at 5.85; and 10 p. p. m. at 5.5. The increasing concentration narrows the coagulation zone. The two samples of pH 5.5 and 5.8 gave no coagulation within 1 hour with 10 p. p. m. of the tartrate. Here, as in the case of the oxalate, there is probably a complex compound formed of aluminum tartrate and aluminum hydroxide, with the resulting properties different from the simple floc.

Table V—Effect of Sodium Oxalate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

$Na_2C_2O_4$—5 P. P. M.		$Na_2C_2O_4$—10 P. P. M.		$Na_2C_2O_4$—20 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.5	42	5.45	41	6.6	40
5.8	25	5.25	18	6.7	30
6.0	14	6.0	12	7.05	23
6.15	9	6.2	8	7.2	15
6.3	8	6.3	8	7.3	12
6.4	7	6.6	7	7.4	12
6.5	6.5	6.7	7	7.65	16
6.6	6.5	6.8	6.5	7.8	26
6.7	6.5	7.0	7	7.85	38
6.8	6.5	7.2	8.5		
7.0	6.5	7.3	9.5		
7.1	7	7.5	12		
7.3	8 5	7.7	17		
7.4	14.5	7.8	40		
7.65	44				

Table VI—Effect of Potassium Tartrate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

$K_2C_4H_4O_6$—5 P. P. M.		$K_2C_4H_4O_6$—7.5 P. P. M.		$K_2C_4H_4O_6$—10 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.1	20	5.15	32	5.0	28
5.45	8	5.5	5	5.2	11
5.5	6.5	5.7	4	5.4	7
5.8	4.5	5.8	4	5.6	5.5
5.9	4	6.05	4	5.9	12
6.2	3.5	6.1	5	6.0	38
6.4	3	6.4	8.5		
6.45	3.25	6.85	31		
6.55	3.5				
6.7	3.75				
6.8	4				
6.95	6.5				
7.0	7				
7.25	25				

Tannic Acid—The presence of small amounts of tannic acid has a marked effect on the time required for coagulation. (Table VII and Graph No. VII) Experience in waterworks operation with such colored waters has led to the conclusion that optimum precipitation takes place at a pH near 5.0 to 5.5. Tannins and tannic acids are negative colloids, and as alum floc is positive it would seem that immediate precipitation would take place if the two were allowed to come in contact. That this is true is shown by the short time required to bring about coagulation as compared with the other substances studied—about 1.5 minutes. Also the coagulum was much larger than in the other types. The pH range is, however, very narrow and well defined. Here again it is more probable that the floc is a complex tannate. As the authors previously mentioned[8 9] were dealing with colored waters, their observations on the optimum pH for coagulation do not fix the isoelectric point of pure alum floc any more

than do the experiments with the oxalate or any of the other salts studied. It does follow, however, that clarification of colored waters, if the color is due to tannic acid or its compounds, would take place in an acid medium, within narrow ranges of hydrogen-ion concentration and the exact point of the optimum results being dependent on the tannin content.

Table VII—Effect of Tannic Acid on Coagulation Time of Alum Floc

$C_{10}H_{14}O_9$— 10 P. P. M.		$C_{10}H_{14}O_9$— 20 P. P. M.		$C_{10}H_{14}O_9$— 35 P. P. M.		$C_{10}H_{14}O_9$— 50 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.5	23	5.1	25	5.0	20	4.75	22
5.7	10	5.3	14	5.3	5.5	4.85	10
5.8	5.5	5.95	3.5	5.5	2.5	5.15	2.5
5.95	4	6.1	3	5.7	1.5	5.45	1.5
6.05	3	6.2	2.5	5.8	1.5	5.43	1.5
6.2	2	6.4	2	6.1	1.5	5.65	2
6.3	2	6.6	2	6.2	1.5	5.85	2.25
6.4	2	6.7	2	6.6	2	6.0	6
6.6	2	6.8	2.8	6.75	9	6.25	28
6.7	2.5	6.9	8	6.85	20		
6.9	3	6.95	16				
7.1	4.5						
6.25	8						
7.45	20						

Table VIII—Effect of Potassium Phosphate on Coagulation Time of Alum Floc

K_3PO_4— 10 P. P. M.		K_3PO_4— 50 P. P. M.		K_3PO_4— 100 P. P. M.		K_3PO_4— 200 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.5	6	6.3	16	6.2	19	6.1	15
6.4	3.5	6.25	8	6.0	8	6.0	9.5
6.25	3.25	6.05	5	5.9	4.5	5.9	7.4
6.15	3	6.0	4.5	5.75	4.5	5.8	6.5
6.0	3.25	5.8	4.4	5.6	3.5	5.7	5.5
5.7	3.5	5.4	5	5.35	4	5.5	5.5
7.45	23	5.0	24	5.15	5.5	5.25	5.5
				4.9	32	5.0	6
						4.9	22

Potassium Phosphate—As shown in Table VIII and Graph No. VIII, here, as in the case of the tartrate, the optimum point is moved to the acid end, from a pH of 6.25 with 10 p. p. m. to pH 5.3, with 20 p. p. m. These are the type of curves used by Theriault and Clark in deducing the isoelectric point of alum floc. From a comparison of preceding graphs it becomes evident that such coagulation curves would not represent the true behavior of pure aluminum hydroxide, but more likely, as with the oxalate and tartrate, of a system of mixed hydroxide and phosphate. There seems to be no connection between the simple alum curve and those obtained with even small concentrations of phosphate.

Table IX—Coagulation of Alum Floc Alone with Sodium Hydroxide

Alum—34 P. P. M.		Alum—51 P. P. M.		Alum—68 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.8	23	6.45	36	5.5	44
7.0	15	6.5	27	6.0	17
7.1	14	6.75	16	6.3	11
7.2	13	6.85	15	6.5	8
7.25	12	7.05	11	6.7	6.5
7.7	13	7.2	9	7.3	4.5
8.0	15	7.3	9	7.7	7
8.2	17	7.6	10	7.8	11
8.5	19	7.7	11	8.3	28
8.75	21	7.85	13	8.5	44
		8.0	19		
		8.25	36		

Alum Sulfate Alone—It is common waterworks practice to control the coagulation behavior by adjusting the alum dosage. In Table IX and Graph No. IX are given the results of the coagulation of three different dosages of alum in solutions of varying pH. It will be observed that the point of optimum coagulation is not materially changed, remaining near 7.25 to 7.35. Increase in alum dosage widens the zone somewhat, principally on the acid side. The time of most rapid coagulation does vary with the alum used, 2 grains per gallon (34 p. p. m.) requiring about one and one-half times as long as 3 (51 p. p. m.) and twice as long as 4 grains (68 p. p. m.).

Summary and Conclusions

One of the chief difficulties in the operation of a water plant is interpretation of the laboratory results to the plant. The effect of constant agitation on the duplication of results was among the first points investigated. A large number of experiments, in which the bottles were shaken for a few seconds to several minutes and allowed to stand during the formation of the floc, did not give results capable of duplication in a single instance. The practice of providing uniform agitation for the laboratory samples is not yet very generally used. One of the major conclusions to be drawn from this investigation seems to be the absolute necessity of some such provision in all waterworks laboratories, and further, coagulation pits should be so designed as to provide such agitation for some time, even after thorough mixing.

For plants which use streams as the source of supply the variation of floc behavior and the difficulty of holding a good floc during flood periods is more probably due to variations in the sulfate content than to variations in the hydrogen-ion concentration.

The abnormal behavior of the oxalate, tartrate, and phosphate ions shows the futility of any attempt to study the action of alum floc with varying pH if the solutions used are buffered with salts. The results so obtained define the point not of minimum stability nor of optimum coagulation of the pure floc, but of a composite of some kind entirely different in its properties. The majority of water plants use waters of hydrogen-ion concentration near neutrality and the fact that alum floc would form at all in such waters is inexplainable in the light of the experiments of Theriault and Clark. As they used solutions buffered with phosphate salts, it has been here shown that their results cannot be interpreted as indicative of the behavior of the pure floc.

Every operator hase xperienced the difficulties in the sudden appearance of color in the raw water. It is almost always difficult to obtain a good floc under such conditions. Operators usually prefer water of a very high turbidity to one of even a slight color. The experiments with tannic

acid show the necessity of providing an acid medium under such circumstances. The optimum coagulation point observed here checks very closely with the points obtained by Baylis and Norcum, who were dealing with soft colored waters. The confirmatory experiments of Theriault and Clark are somewhat of an accident.

It must be concluded, therefore, that each water purification plant must determine the conditions of optimum floc formation for the water with which it is dealing and conclusions drawn from the operation of one plant are not applicable to another if the salt content of the water is different; also that the gelatinous material commonly thought to be aluminum hydroxide is a very complex substance, the properties of which vary widely with slight changes in the surrounding medium; and that the hydrogen-ion concentration is less of a controlling factor than the salt content of the water.

VITA

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